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Metastable spin-polarized carbon clusters C_8 and their ensembles

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Results of tight-binding calculations on metastable spin-polarized carbon clusters C_8 (prismanes) are presented. It is shown that those clusters can form ensembles due to intercluster bonding. The binding energy of a given metastable configuration decreases monotonously with the total spin S , while the activation energy for the decay of a metastable state has distinct maxima as a function of S . For specific values of S , the dynamical stability of spin-polarized ensembles of prismanes appears to be higher than that of an isolated prismane, pointing to a possibility of existence of "cluster matter" composed of spin-polarized clusters C_8 .

1. Introduction

Carbon is a chemical element with a great number of unique properties. In particular, carbon is known by its polymorphism. Due to its ability to exist in different valence states, carbon can form a rich variety of compounds, including diamond, graphite, carbyne, etc. In the field of nanostructures, cage-like fullerenes (C_{60} etc. [1]) attract much attention due to their both practical and fundamental importance. Recently, the cage-like cluster C_{20} was synthesized [2]. This cluster is the smallest possible fullerenes cage consisting of 12 pentagons. First-principle calculations [3] point to a possibility of synthesis of condensed C_{20} phases with three-dimensional

covalent networks.

In recent numerical simulations of small carbon clusters, a possible existence of another cage-like cluster C_8 (prismane) was suggested theoretically [4]. Prismane was predicted to have the shape of a six-atom triangular prism with two excess atoms above and below its bases, see Fig.1. There is a good reason to believe that prismane C_8 is the smallest possible *three-dimensional* carbon cluster. Prismane is the *metastable* cluster. Its binding energy E_b (defined as $E_b(N) = NE(1) - E(N)$, where $E(N)$ is the total energy of an N -atom cluster, $E(1)$ is the energy of an isolated carbon atom) was calculated to be 5.1 eV/atom [4], i.e., 0.45 eV/atom lower than the binding energy of the stable one-dimensional eight-atom cluster and 2.3 eV/atom lower than the binding energy of the bulk graphite or diamond. It is essential, however, that the calculated value of the lowest energy barrier that prevents the prismane from decay into the stable or another metastable atomic configurations with greater values of E_b appears to be rather high, about 0.44 eV [5], resulting in a rather long lifetime of the prismane even at room temperature. Hence, it is likely that this cluster may be observed experimentally.

Since the prismane had been predicted [4], the bonding between prismanes was studied and several configurations in which prismanes form metastable ensembles were found [6, 7, 8]. In those ensembles, the inter-prismane bonds are rather strong, so that one could expect prismanes C_8 to form a covalent solid. However, the stability (and hence, the lifetime) of the prismane-based ensembles was shown to decrease strongly with the number of prismanes in the ensemble.

Until now, theoretical studies of prismanes and their ensembles were restricted to the non-polarized case, i.e., the total spin S of the systems under consideration was assumed to be zero [4, 5, 6, 7, 8]. Meanwhile, the polarization of small species of

substance (including molecules and clusters) can increase the stability of the system and/or result in the formation of new metastable configurations. For example, two helium atoms, being in the ground state with $S = 0$ each, do not form the covalently bound molecule He_2 , while the existence of metastable long-lived molecule He_2^* in the excited state with $S = 1$ has been demonstrated both theoretically [9] and experimentally [10]. In general, one can expect that the binding energy of the system composed of nonmagnetic atoms decreases with S , and hence spin-polarized clusters and their ensembles can be considered as candidates to the so called high energy density materials (HEDM). The question is whether the lifetimes of such systems are long enough for they could be synthesized, investigated and used in practice. So, the study of metastable spin-polarized atomic configurations is of great fundamental interest and practical importance.

In this paper, we extend our previous studies to the case of spin-polarized prismanes C_8 and their ensembles. We show that metastable prismane-like carbon clusters with $S \neq 0$ can exist and form ensembles due to intercluster bonding. The binding energies and the activation energies for the decay of metastable states are calculated as functions of S for an isolated prismane and different arrangements of prismanes in the ensembles.

2. Computational details

The search for metastable configurations of prismane-like carbon clusters and their ensembles with different spins S was carried out by means of structural relaxation technique. Starting with a particular atomic arrangement, all atoms were allowed to displace step by step in the directions of interatomic forces, atomic velocities being terminated at each step. The forces were determined via calculation of the

total energy of the system (or, equivalently, the binding energy) making use of a transferable tight-binding potential [11, 12] that had been proven to reproduce accurately the energy-versus-volume diagram of carbon polytypes and to give a good description of both small clusters and bulk structures of carbon [11, 12]. This potential has been used for simulations of metastable prismane-like structures with $S = 0$ in our previous works [4, 5, 6, 7, 8]. The numerical technique employed is not as sophisticated and time-consuming as *ab initio* ones and allows for molecular dynamics simulations of rather large systems for a relatively long time.

Depending on the choice of initial configuration, the resulting atomic arrangement corresponds to either global or local minimum of the total energy as a function of atomic coordinates for a given number of atoms in the system (stable and metastable states, respectively). We were interested in *metastable states* separated from the stable and/or other low-lying metastable configurations by the energy barriers. An important characteristic of a metastable configuration is the activation energy E_a for its decay. For a given temperature T , the value of E_a determines the probability of the system decay in a unit of time,

$$W \propto \exp(-E_a/k_B T), \quad (1)$$

and hence the lifetime τ of a particular metastable state is

$$\tau \propto \tau_0 \exp(E_a/k_B T), \quad (2)$$

where k_B is the Boltzmann constant, τ_0 is a characteristic time of the order of an oscillation period of the system ($\sim 10^{-13}$ s for the C_8 clusters and their small ensembles).

The lifetimes τ at different temperatures were calculated directly by molecular dynamics simulation of thermally isolated systems. Since the cluster decay is prob-

abilistic in nature, we accumulated a great statistics ($30 \div 100$ trials) in order to get a reliable estimate of the value of E_a through fitting the results obtained to Eq. (2).

3. Results and discussion

To find three-dimensional spin-polarized prismane-like configurations of eight carbon atoms, we made use of the non-polarized prismane structure [4] as an initial atomic arrangement in the structural relaxation procedure. We have found three-dimensional metastable C_8 configurations for $S = 1 \div 7$, while for $S > 7$ all relaxed structures appeared to be either one- or two-dimensional. Metastable configurations can be subdivided into "nondistorted" ($S = 0, 4, 7$) and "distorted" ($S = 1, 2, 3, 5, 6$) ones. The structure of nondistorted prismanes is characterized by three different bond lengths a, b, c (symmetrical configuration), see Fig.1. In distorted prismanes, the bond lengths are slightly scattered around those three characteristic lengths, see Fig.2. From Fig.2 one can see that the values of a, b , and c (or their average values for distorted configurations) increase with S , so that the cluster volume increases with S .

The binding energy E_b of spin-polarized prismanes strongly decreases with S from $E_b = 5.1$ eV/atom at $S = 0$ down to $E_b = 2.1$ eV/atom at $S = 7$, see the lower curve in Fig.3. Hence, the energy E_{acc} accumulated in metastable prismanes increases considerably and exceeds 5 eV/atom at $S = 7$ (here $E_{acc} = E_b^{graphite} - E_b$, where $E_b^{graphite} = 7.4$ eV/atom is the binding energy of graphite or diamond, the most stable carbon structures that are characterized by the maximum value of E_b per atom). Such an energy could be released upon fusion of a large number of prismanes into the bulk specimen with the graphite structure, accompanying by the spin-depolarization transition (i.e., the reduction of the total spin down to $S = 0$).

Fig.4 shows the dependence of activation energy E_a for the decay of metastable spin-polarized prismane C_8 versus the total spin S . One can see that the value of E_a is maximum, $E_a = (0.84 \pm 0.05)$ eV, for the non-polarized prismane C_8 with $S = 0$. An estimate of the lifetime τ making use of Eq. (2) gives $\tau \sim 1$ s at $T = 273$ K (see also Ref. [4]), the value of τ being increased exponentially with decreasing T . For spin-polarized C_8 configurations, the value of E_a is $4 \div 12$ times lower than that for $S = 0$. Note that the dependence of E_a on S in the range $S = 1 \div 7$ is nonmonotonous and has local maxima at $S = 4$ and $S = 7$.

In attempts to get a physical insight into the nonmonotonous dependence of E_a versus S , we have calculated the difference $\Delta = E_{LUMO} - E_{HOMO}$ between the energies of the lowest unoccupied and the highest occupied molecular orbitals as a function of S . The results are shown in Fig.5. One can see that the curve $\Delta(S)$ has maxima at $S = 0, 4$, and 7 , in accordance with higher values of E_a for those values of S , see Fig.4.

Now we turn to small ensembles composed of spin-polarized prismanes C_8 . We have studied various arrangements of two prismanes C_8 with respect to each other and found four different metastable configurations $(C_8)_2$. They are shown in Fig.6. In configuration A, the intercluster bonding occurs via "top atoms", so that there is a single inter-cluster bond. In configurations B and C, there are two inter-cluster bonds between "edge atoms", while in configuration D, there are four inter-cluster bonds (the rectangular facets of the prismanes are parallel). Note that prismanes in the ensembles $(C_8)_2$ preserve their overall original shape, they do not merge into a new cluster C_{16} and survive as the "building blocks" of the ensembles.

For either of four configurations $(C_8)_2$ shown in Fig.6, we have restricted our studies to the range $S = 0 \div 10$. We have found that the metastable configuration

A exists at all values of $S = 0 \div 10$, while the configurations B, C, and D are metastable, respectively, at $S = 0$ and 7; 6 and 7; 8 and 9 only. The binding energy E_b of $(C_8)_2$ ensembles monotonously decreases with S from $E_b = 5.2$ eV/atom at $S = 0$ down to $E_b = 3.4$ eV/atom at $S = 10$, see the middle curve in Fig.3. The value of E_b at a given S is almost the same in different metastable configurations $(C_8)_2$, if any.

Although at $S \neq 0$ the curve $E_b(S)$ for the ensembles $(C_8)_2$ lies well above that for the prismane C_8 , see Fig.3, a close inspection of those curves shows that the binding energy $E_b(2S)$ of an ensemble $(C_8)_2$ composed of two prismanes C_8 with the spin S each is almost the same as the binding energy $E_b(S)$ of an isolated prismane C_8 with the spin S , being higher by just $(0.1 \div 0.2)$ eV/atom for all values of S considered. Hence, the energy $E_{acc} = E_b^{graphite} - E_b$ accumulated in two metastable prismanes C_8 changes insignificantly upon formation of the ensemble $(C_8)_2$. A small increase in E_b by $(0.1 \div 0.2)$ eV/atom is due to appearance of new covalent bonds between two prismanes C_8 and, as a consequence, the decrease of the total energy of the system. The bond energy is about 1 eV/bond.

In contrast to the prismane C_8 , the activation energy E_a for the decay of the ensemble $(C_8)_2$ in configuration A as a function of S has a broad maximum, $E_a = (0.35 \pm 0.05)$ eV, at $S = 6 \div 8$, while the value of E_a for the non-polarized ensemble $(C_8)_2$ with $S = 0$ is very low, $E_a \approx 0.03$ eV, see Fig.7. (We recall that in the prismane C_8 , the maximum of the $E_a(S)$ curve is at $S = 0$). For other metastable $(C_8)_2$ configurations shown in Fig.6, the value of E_a equals to (0.83 ± 0.12) eV and (0.12 ± 0.03) eV for configuration B with $S = 0$ and 7 respectively; (0.03 ± 0.005) eV and (0.29 ± 0.03) eV for configuration C with $S = 6$ and 7 respectively; (0.1 ± 0.03) eV and (0.07 ± 0.01) eV for configuration D with $S = 8$ and 9 respectively. It is

worth noting that several spin-polarized configurations $(C_8)_2$ with specific values of S appear to be more stable than constituting spin-polarized prismanes C_8 , c.f. Figs. 4 and 7.

We have also studied the metastability of quasi-one-dimensional spin-polarized ensembles $(C_8)_3$ formed upon attachment of a third prismane C_8 to the ensemble $(C_8)_2$ in configuration A, see Fig.8. We have restricted ourselves to the range $S = 0 \div 16$. We have found that the metastable configuration $(C_8)_3$ exists at all values of S in this range. The binding energy E_b of the $(C_8)_3$ ensemble monotonously decreases with S from $E_b = 5.3$ eV/atom at $S = 0$ down to $E_b = 3.3$ eV/atom at $S = 16$, see the upper curve in Fig.3. From Fig.3 one can find that the binding energy $E_b(3S)$ of an ensemble $(C_8)_3$ composed of three prismanes C_8 with the spin S each exceeds the binding energy $E_b(S)$ of an isolated prismane C_8 with the spin S by ≈ 0.2 eV/atom for all values of S in the range $S = 1 \div 5$. Hence, an increase in the number m of prismanes in a metastable spin-polarized ensemble $(C_8)_m$ leaves the energy $E_{acc} = E_b^{graphite} - E_b$ accumulated in the ensemble almost unchanged.

The shape of the curve $E_a(S)$ for the ensemble $(C_8)_3$ is similar to that for the ensemble $(C_8)_2$, see Fig.7. Note, however, that the maximum of $E_a(S)$ for the ensemble $(C_8)_3$ is shifted to greater values of $S = 9, 10$ and is higher by ≈ 0.1 eV than in the case of the ensemble $(C_8)_2$. So, the stability (and hence, the lifetime) of the system increases with the number of prismanes in the ensemble.

Fig.9 shows the activation energy E_a versus the difference $\Delta = E_{LUMO} - E_{HOMO}$ between the energies of the lowest unoccupied and the highest occupied molecular orbitals for all metastable configurations considered in this work. One can see the overall increase of E_a with Δ . Such a correlation between E_a and Δ indicates that the nonmonotonous dependence of E_a on S stems from the nonmonotonous

dependence of Δ on S .

4. Conclusions

We have numerically examined a possibility of existence of a spin-polarized cage-like metastable carbon cluster prismane C_8 and small ensembles composed of those clusters. We have shown by molecular dynamics simulations that the activation energy E_a for the decay of a metastable configuration is a nonmonotonous function of the total spin S of the system and has maxima at certain values of S . The most stable structures are characterized by the large energy gap between the lowest unoccupied and the highest occupied molecular orbitals. The maximum value of E_a increases with the number of prismanes in the ensemble, pointing to a possibility of existence of "cluster matter" composed of spin-polarized clusters C_8 . The metastable ensembles of prismanes C_8 accumulate a great amount of energy (several eV/atom) that may be released upon fusion of a large number of prismanes into the bulk specimen. Hence, such ensembles can be considered as candidates to the high energy density materials (HEDM). The role of spin-flip processes for the stability of spin-polarized cluster configurations needs further consideration.

Acknowledgments

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Figure captions

Fig.1. Metastable prismane C_8 . For $S = 0, 4$, and 7 the prismane structure is characterized by three different bond lengths $a=AE=BF=CG$, $b=AD=BD=CD=EH=FG=GH$, and $c=AB=AC=BC=EF=EG=FG$ (symmetrical configuration). For other values of S , the prismane is slightly distorted, see text and Fig.2 for details. $a = 1.28 \text{ \AA}$, $b = 1.47 \text{ \AA}$, $c = 2.31 \text{ \AA}$ for $S = 0$.

Fig.2. Bond lengths a (circles), b (triangles), and c (squares) of metastable prismane configurations versus the total spin S , see Fig.1 for the definition of a, b, c . For the distorted configurations with $S = 1, 2, 3, 5, 6$ there are more than three different bond lengths, i.e., some of equalities $AE=BF=CG$, $AD=BD=CD=EH=FG=GH$, $AB=AC=BC=EF=EG=FG$ are violated.

Fig.3. Binding energy E_b of the metastable prismane C_8 (closed circles), see Fig.1, the metastable ensembles $(C_8)_2$ in configurations A (closed triangles), B (open circles), C (open squares), D (open triangles), see Fig.6, and the metastable ensemble $(C_8)_3$ (closed squares), see Fig.8 versus the total spin S of the system. Lines are the guides to the eye.

Fig.4. Activation energy E_a for the decay of the metastable prismane C_8 versus the total spin S . Line is the guide to the eye.

Fig.5. The difference $\Delta = E_{LUMO} - E_{HOMO}$ between the energies of the lowest unoccupied and the highest occupied molecular orbitals of the metastable prismane C_8 versus the total spin S . Line is the guide to the eye.

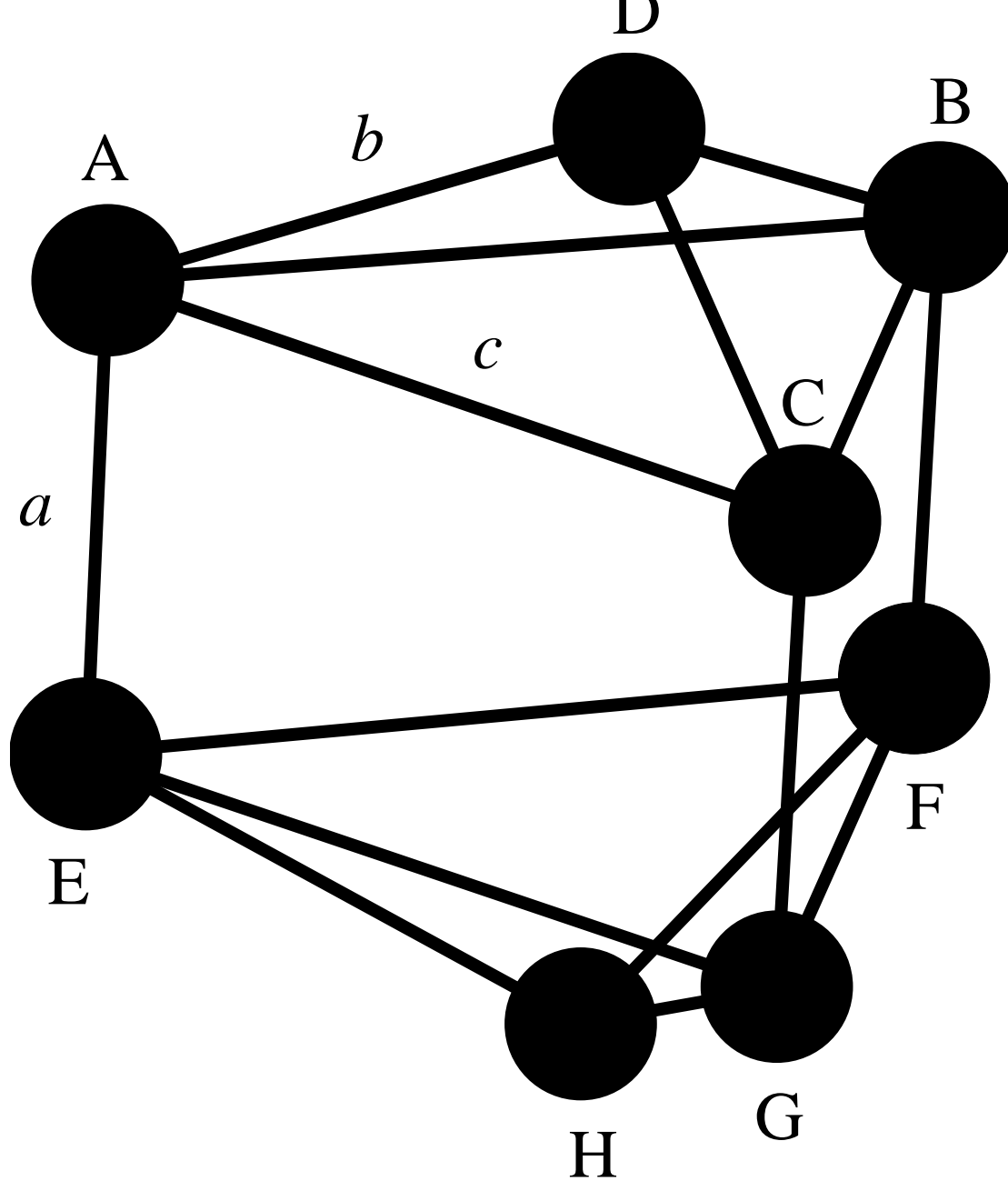
Fig.6. Four different configurations (A, B, C, D) of metastable ensembles $(C_8)_2$.

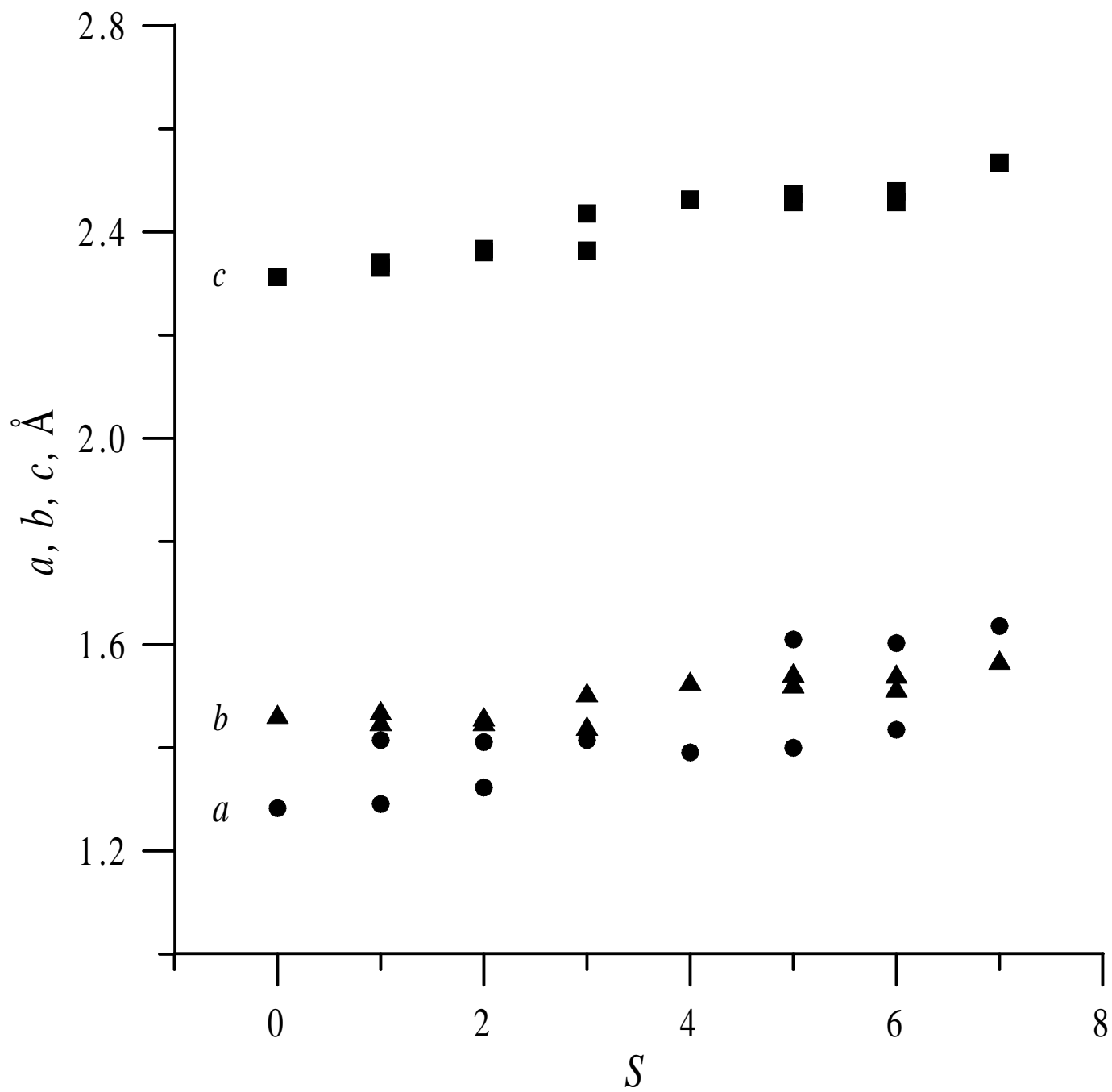
Fig.7. Activation energy E_a for the decay of the metastable ensemble $(C_8)_2$ in configuration A (circles), see Fig.6a, and quasi-one-dimensional ensemble $(C_8)_3$ (triangles), see Fig.8, versus the total spin S of the system. Lines are the guides to the

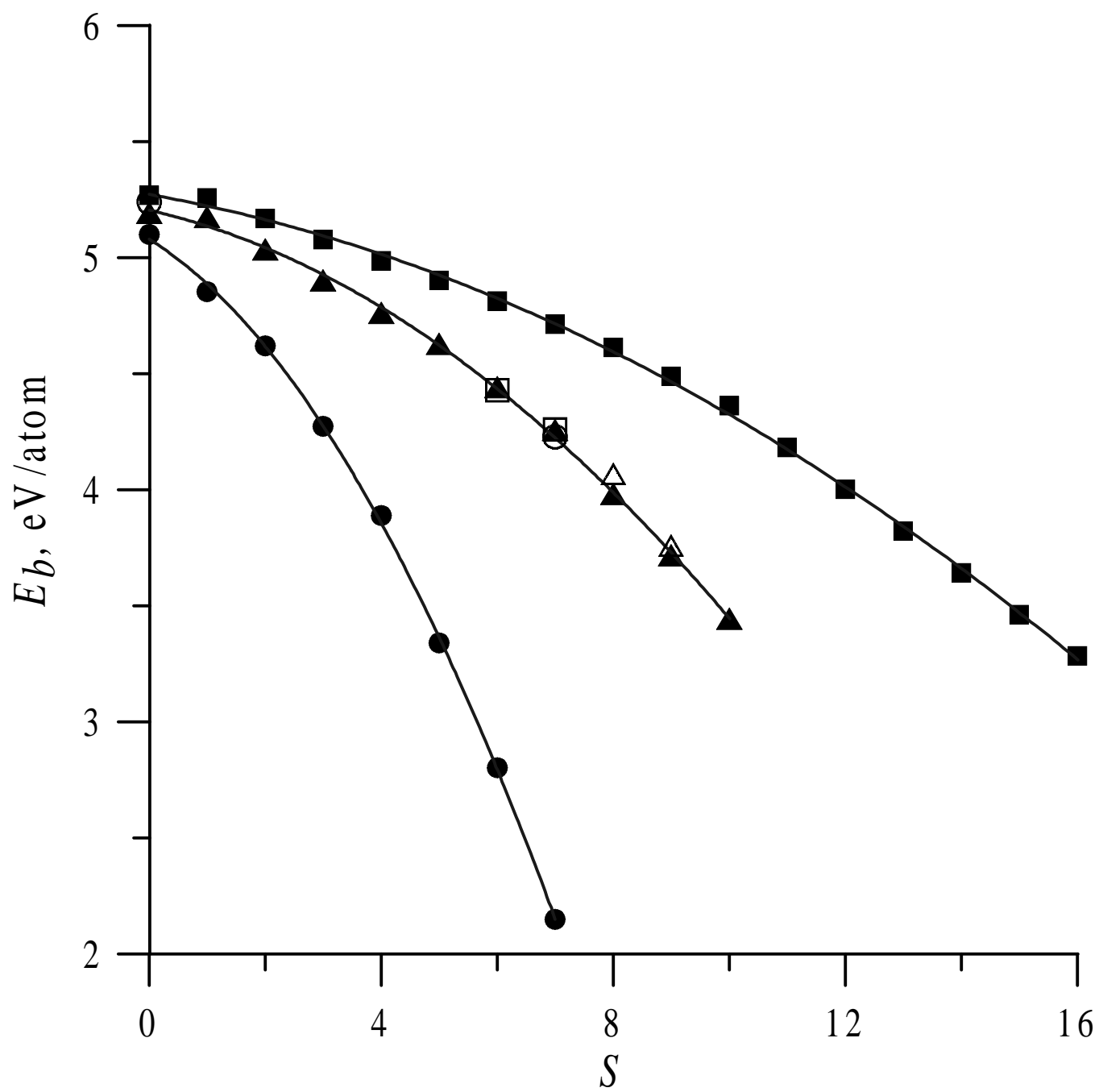
eye. Two values of E_a of the ensemble $(C_8)_2$ at $S = 1$ correspond to two basically different paths of the ensemble decay.

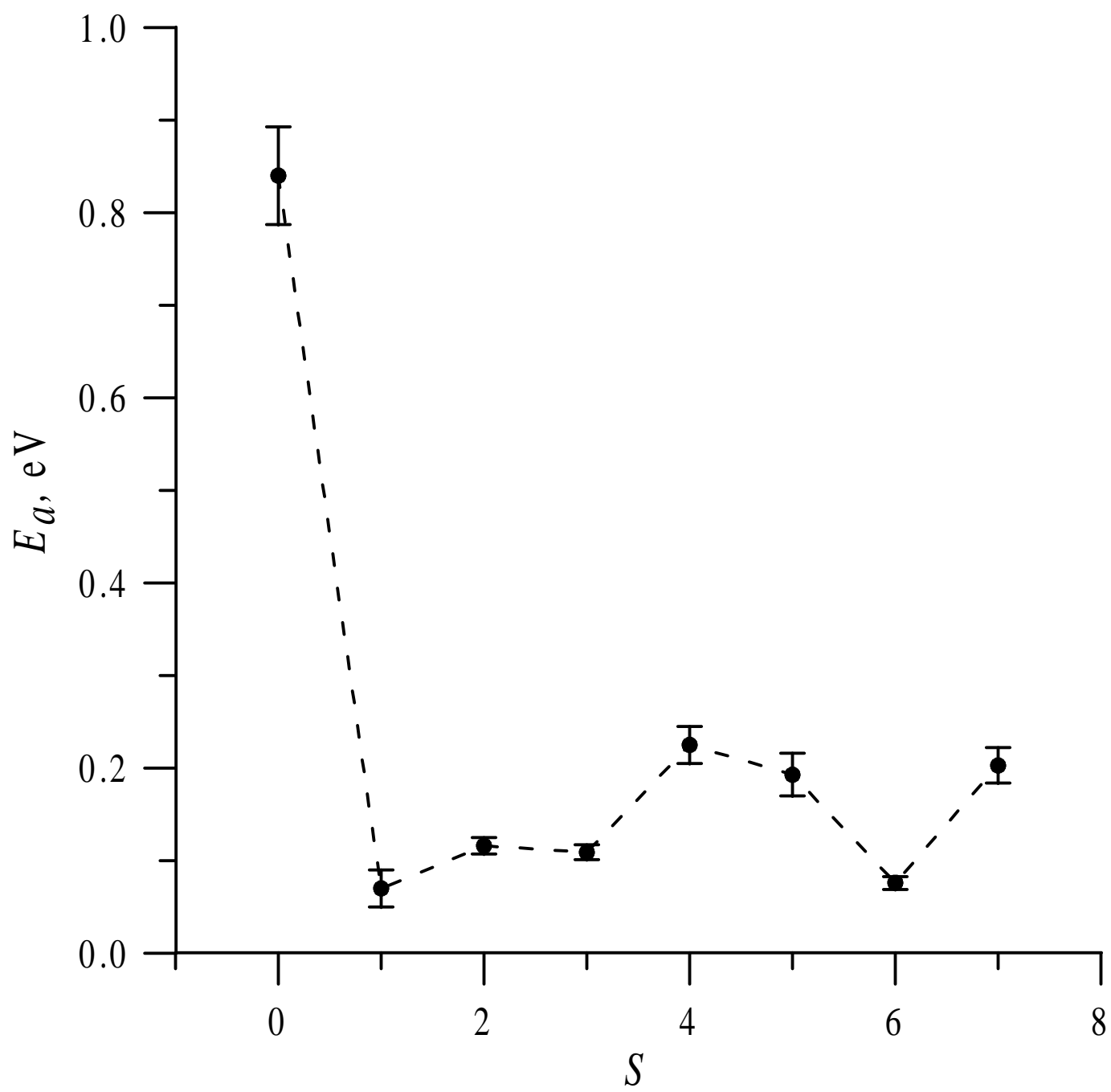
Fig.8. Quasi-one-dimensional metastable ensemble $(C_8)_3$.

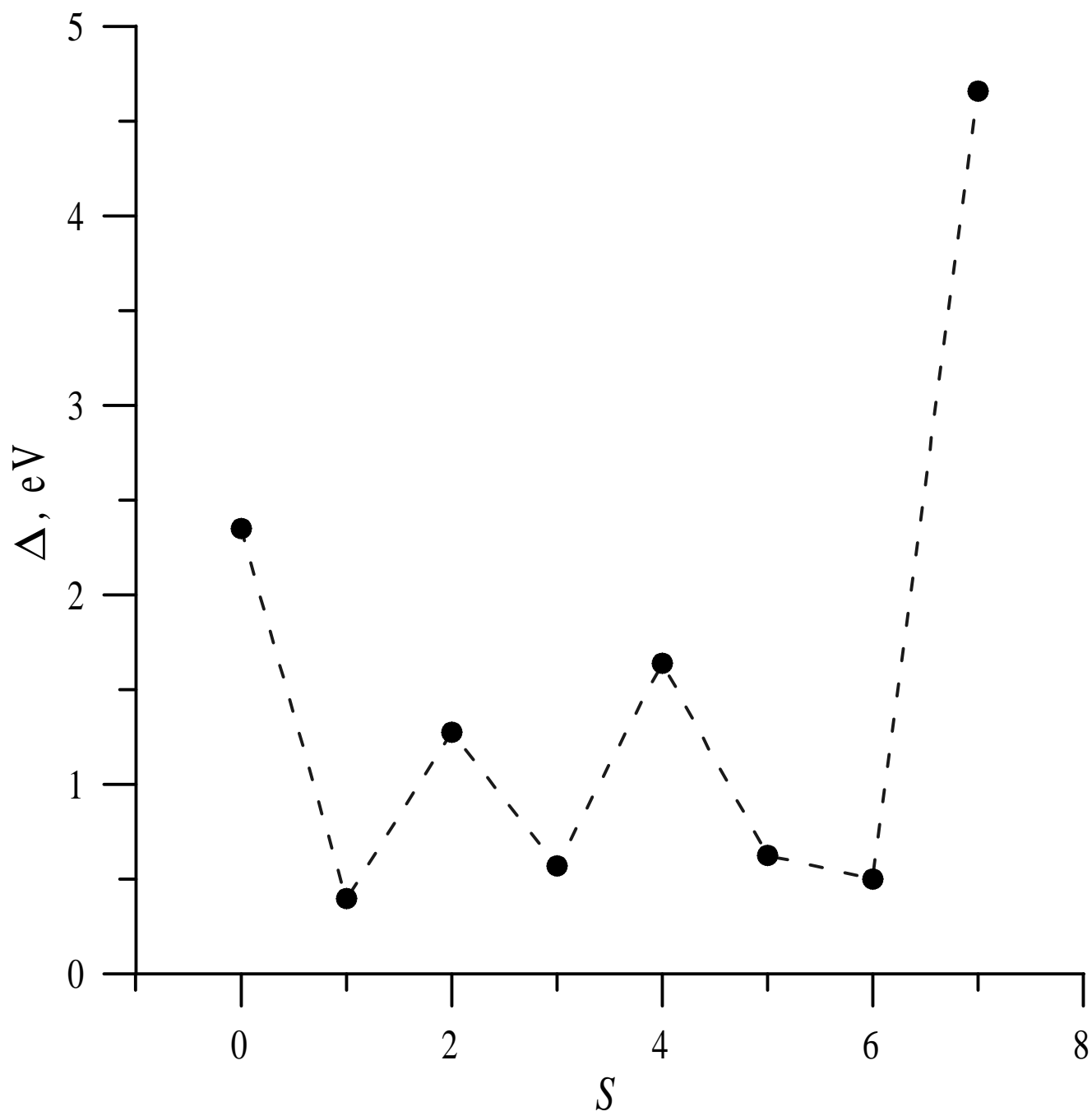
Fig.9. Activation energy E_a for the decay of metastable spin-polarized configurations versus the difference $\Delta = E_{LUMO} - E_{HOMO}$ between the energies of the lowest unoccupied and the highest occupied molecular orbitals for the metastable prismane C_8 (closed circles), the metastable ensembles $(C_8)_2$ in configurations A (closed triangles), B (open circles), C (open squares), D (open triangles), and the metastable ensemble $(C_8)_3$ (closed squares).



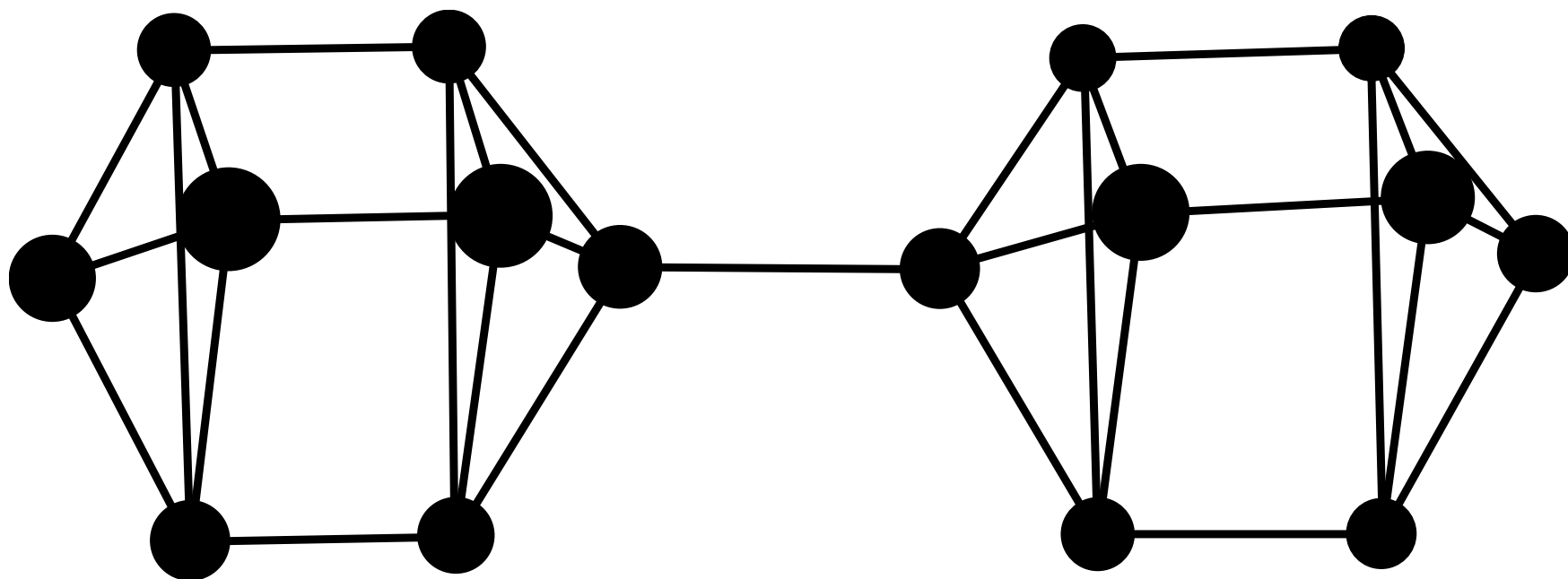




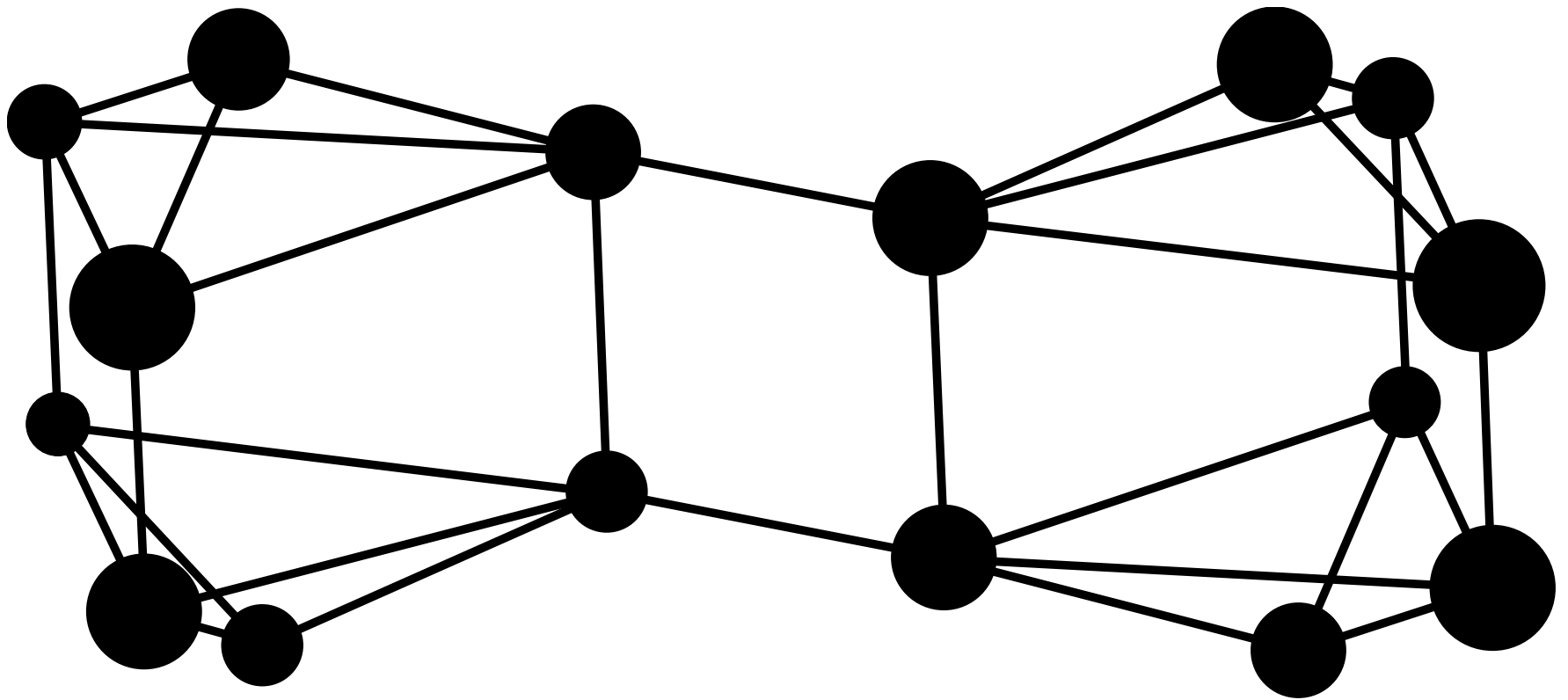




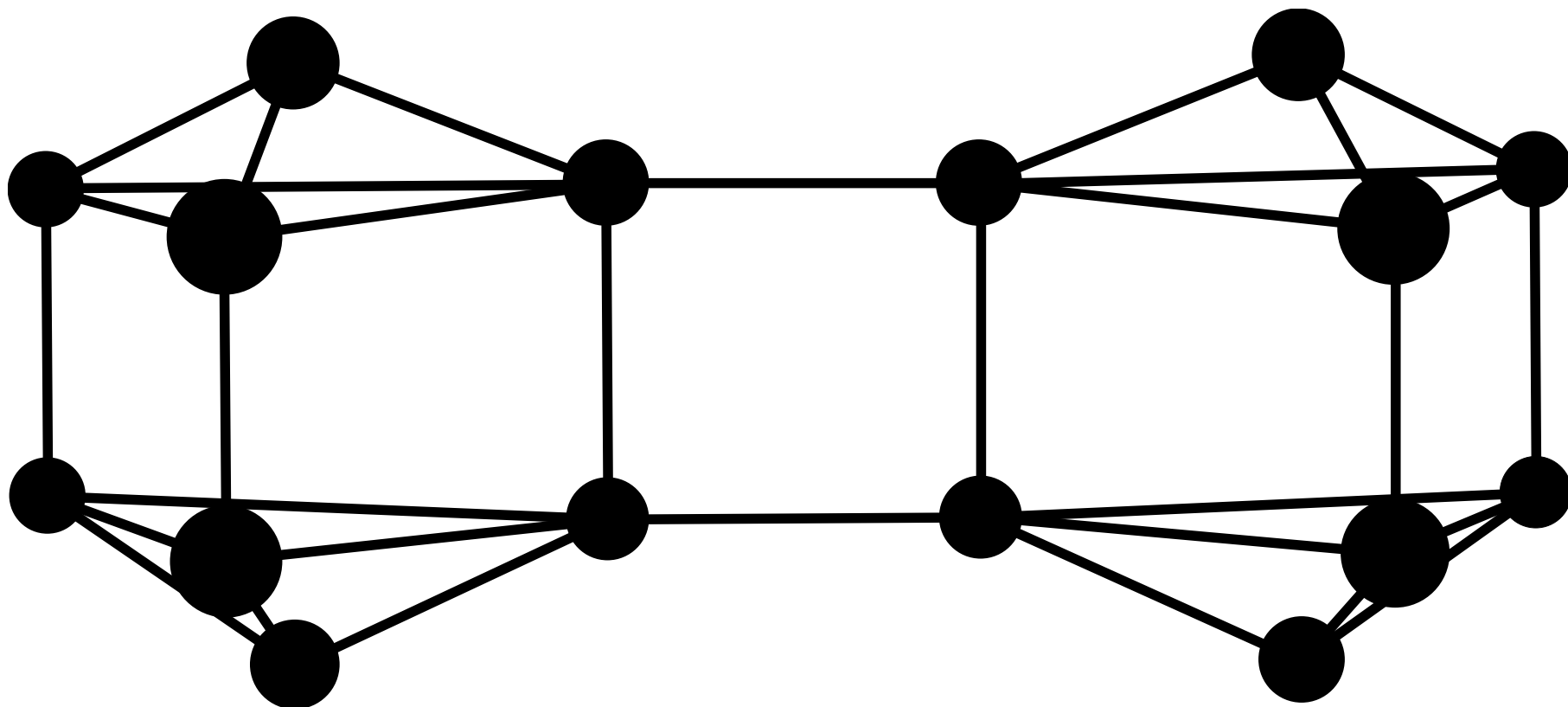
A



B



C



D

